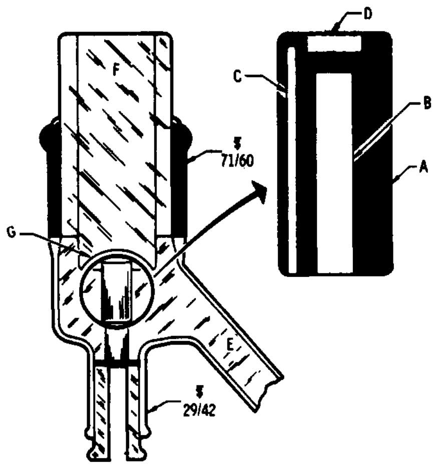

Figure 1. Heating stage and collector assembly—evaporation rate apparatus

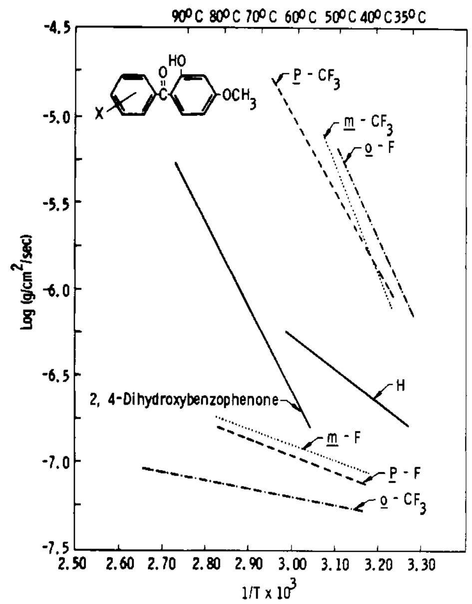

Figure 2. Evaporation rates

by using the stage as a melting point block for zone-refined samples in the range 50° to 150° C. The precision of the stage temperature was judged to be ± 0.5° C.

DISCUSSION

As the area of the sample depression, the temperature, and the amount of material transferred per second were known, the vapor pressure was determined by using the equation

$$P_{\mathrm{mm}} = 17.14G(T/M)^{1/2}$$

where P_{mm} is the vapor pressure in millimeters of mercury, G is the evaporation rate in grams per square centimeter per second, M is the formula weight, and T is the absolute temperature (*1*). The data are given in Table I and Figure 2. The volatilities of 2-hydroxy-4-methoxy-3′-fluorobenzophenon , 2-hydroxy-4-methoxy-4′-fluorobenzophenone, and 2-hydroxy-4-methoxy-2′-trifluoromethylbenzophenone are lower than 2,4-dihydroxybenzophenone and 2-hydroxy-4-methoxybenzophenone at temperatures above 60° C. Figure 2 indicates that the vaporization rate of 2,4-dihydroxybenzophenone will exceed that of 2-hydroxy-4-methoxybenzophenone at temperatures higher than 342° K. (69° C.). Such an extrapolation is not valid, however, since these data are for evaporation rates of solid samples and 2-hydroxy-4-methoxybenzophenone will be liquid at temperatures above 65° C. An evaporation curve for the liquid will have an entirely different slope.

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Dielectric Properties of Phosphoric Acid Solutions at 25° C.

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MATHEMATICAL DESCRIPTIONS of the absorption-dispersion phenomena of electrolytic solutions have been derived from measurements of their dielectric properties (*3-7*). The present measurements were made to determine the static dielectric constants of phosphoric acid solutions; previously developed mathematical expressions were used in the treatment of the data. Similar measurements were made on sodium chloride solutions to establish the validity of the results by comparison with published values of the static dielectric constants.

EXPERIMENTAL

Phosphoric acid solutions were prepared by dilution of concentrated stock acid that had been purified by crystallization as $2H_3PO_4 \cdot H_2O$; concentrations were established by density (*2*). Sodium chloride solutions were prepared by weight from conductance water and dried reagent-grade salt. The conductance of the water did not exceed 2×10^{-6} ohm^{-1}cm.$^{-1}$, and all calculations were based on the 1961 atomic weights (*11*). The low-frequency conductance of phosphoric acid (*13, 16*) and sodium chloride solutions (*1*) has been reported.

Measurements were made of the microwave transmission characteristics at 25° C. and 3, 10, and 17 Gc. of 0.01 to 95.8 m H_3PO_4 solutions and the results were extrapolated to zero frequency by the Debye arc function to obtain the static dielectric constants, ϵ_o, of the solutions. With increasing concentration, ϵ_o decreased from 78 for water to a minimum of 19 for 65 m H_3PO_4. Results of similar measurements on NaCl solutions were in good agreement with published values for the static dielectric constants.

The microwave transmission characteristics of the test solutions were measured at 3.0000, 9.9987, and 17.0000 Gc. (all ±0.001%) in Harris-O'Konski (*9*) microwave interferometers, one for each frequency, that were modified to minimize undesired reflections. A block diagram of the system is shown in Figure 1. Slide-screw tuner X_1 cancelled reflections of the reference wave, and slide-screw tuners X_2 and X_3 cancelled those of the transmitted wave (X_3 was required only with the 3-Gc. interferometer). The cells for the test solutions (Figure 2) were designed to permit variations in the cell thickness in a constant assembled length, but, because of limitations in the microwave power source, only the thinnest cell of each interferometer was used. The cell and the transmission loop were maintained at 25° ±0.1° C. in an air thermostat.

With a microwave interferometer, the transmission characteristics of a solution are determined from two parameters: the voltage standing wave ratio (VSWR), and the position of a selected point of minimum power within the transmission loop. These parameters were established by locating (Figure 3) the positions of two points, y_1 and y_2, at which the power was the same and which were equidistant from the node at y. The guided wavelength, λ_1, was established for each frequency by measuring the distance between points of minimum power. The method of calculating the VSWR is illustrated in Figure 3. When $n = 2$, the equation corresponds to that of von Hippel (*14*) for the 3-db or "twice minimum power" method. The equation in Figure 3 is valid for all values of n.

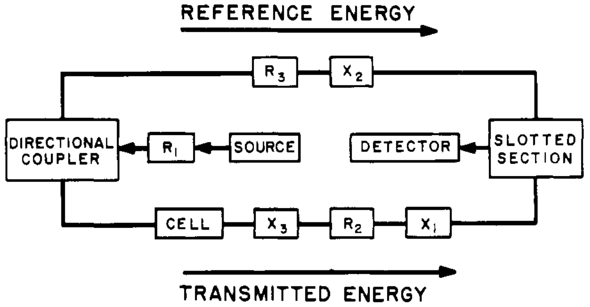


Figure 1. Diagram of microwave interferometer, modified to minimize undesired reflections. R's are attenuators, X's are slide-screw tuners

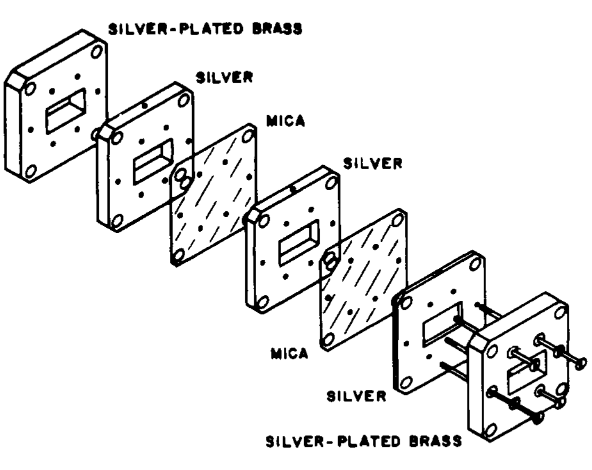


Figure 2. Constant-length assembly, variable-thickness cell

For a given frequency, guided wavelength, and cell thickness, the parameters C and $(y - y_o)$ of Harris and O'Konski (*9*) express the relationships of the VSWR and the position of the node when the cell is filled with test solution to those when the cell is filled with air. Hence, the transmission characteristics are relative to those of air. To facilitate conversion of these parameters to those of ϵ' (the microwave dielectric constant) and ϵ''_{obs} (the observed loss factor), corresponding values of C and $(y - y_o)$ were calculated for selected values of ϵ' and ϵ''_{obs}, and survey charts, such as the one in Figure 4, were constructed. Values of ϵ' and ϵ''_{obs} corresponding to experimental values of C and $(y - y_o)$ were obtained by interpolation on the survey chart.

The dielectric loss factor ϵ''_{ac} was obtained from the relationship

$$\epsilon''_{ac} = \epsilon''_{obs} - \epsilon''_{dc}$$

in which

$\epsilon''_{dc} = 2\sigma/\nu$, the ionic loss

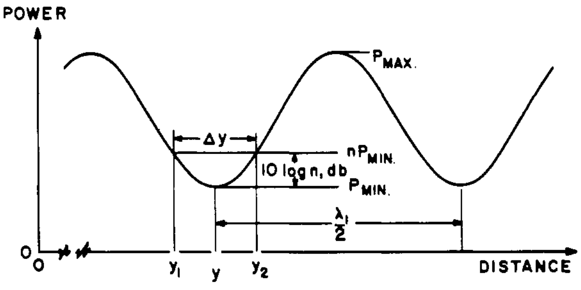
σ = electric conductance, statohm^{-1} cm.$^{-1}$

ν = frequency, cycles sec.$^{-1}$

RESULTS

The microwave dielectric properties of the phosphoric acid and sodium chloride solutions are shown in Table I.

Investigators who have measured dielectric properties have used a number of theoretical and empirical relationships to express the absorption and dispersion phenomena they observed in different media. In the present work, only three frequencies were used; these were too few to define the relationship between the dielectric properties and the frequency so that the results could be extrapolated to zero frequency to determine the static dielectric constant. It was assumed that one or more relationships found by previous investigators to apply to electrolytic solutions would apply also to phosphoric acid solutions, and three of these relationships were tested. Extrapolations by the



$$\text{VSWR} = \sqrt{\frac{P_{MAX.}}{P_{MIN.}}} = \sqrt{1 + \frac{n-1}{\sin^2 \frac{\pi \Delta y}{\lambda_1}}}$$

Figure 3. Power standing wave and equation for voltage standing wave ratio

Table I. Microwave Dielectric Properties of Phosphoric Acid and Sodium Chloride Solutions at 25° C. with Water Reference Based on Debye Semicircle

	3 Gc.[a]					10 Gc.[b]					17 Gc.[c]				
H_3PO_4, m	C	$y - y_o$, cm.	ϵ'	ϵ''_{obs}	ϵ''_{ac}	C	$y - y_o$, cm.	ϵ'	ϵ''_{obs}	ϵ''_{ac}	C	$y - y_o$, cm.	ϵ'	ϵ''_{obs}	ϵ''_{ac}
0.00	0.3784	−3.50	76.6	11.04	11.04	0.0878	−1.514	63.06	29.88	29.88	0.0924	−0.544	46.61	36.53	36.53
0.01	0.3547	−3.43	75.9	12.6	11.6	0.0870	−1.509	62.7	30.0	29.7	0.0916	−0.533	44.9	36.6	36.4
0.10	0.2929	−3.30	74.3	16.9	10.7	0.0823	−1.499	61.7	31.2	29.4	0.0898	−0.527	43.9	37.0	35.9
0.25	0.2345	−3.21	73.0	22.6	10.9	0.0758	−1.482	60.0	32.9	29.4	0.0881	−0.520	42.8	37.4	35.3
0.50	0.1741	−3.11	71.0	31.1	11.9	0.0676	−1.457	57.7	35.2	29.5	0.0860	−0.509	41.1	37.8	34.4
0.75	0.1379	−3.05	69.2	38.7	12.5	0.0615	−1.432	55.5	37.0	29.1	0.0843	−0.499	39.6	38.1	33.5
1.00	0.1117	−3.01	67.6	46.2	12.8	0.0561	−1.411	53.5	38.8	28.8	0.0826	−0.490	38.3	38.4	32.5
1.25	0.0936	−2.97	65.6	52.7	12.3	0.0516	−1.390	51.6	40.4	28.3	0.0810	−0.482	37.0	38.7	31.6
1.50	0.0790	−2.94	63.7	59.3	12.1	0.0475	−1.371	49.7	41.9	27.8	0.0794	−0.475	35.9	39.0	30.7
2.00	0.0589	−2.90	59.8	71.1	10.8	0.0409	−1.340	46.9	44.6	26.5	0.0766	−0.461	33.8	39.4	28.8
3.0	0.0352	−2.89	52.9	93.7	9.1	0.0317	−1.289	41.8	49.2	23.8	0.0712	−0.437	30.2	40.3	25.4
5.0	0.0186	−2.91	41.0	123.9	5.3	0.0225	−1.211	34.1	54.5	18.9	0.0654	−0.400	24.8	40.7	19.8
7.5	0.0136	−2.91	32.9	139.1	2.1	0.0188	−1.149	28.6	56.5	15.4	0.0668	−0.377	22.1	39.2	15.0
10.0	0.0131	−2.87	30.1	139.9	0.5	0.0189	−1.105	25.9	55.2	13.4	0.0710	−0.363	20.9	37.4	12.8
15.0	0.0166	−2.69	28.8	124.3	−1.1	0.0238	−1.031	23.5	48.8	11.2	0.0866	−0.336	19.2	32.4	10.3
20.0	0.0221	−2.46	26.6	106.5	−1.8	0.0317	−0.967	22.1	42.2	9.7	0.1068	−0.314	18.1	27.8	8.7
30.0	0.0337	−2.14	23.9	83.4	0.5	0.0501	−0.872	20.1	32.8	7.9	0.1455	−0.284	16.8	21.5	6.9
50.0	0.0564	−1.79	21.6	59.8	0.3	0.0850	−0.774	18.0	23.6	5.8	0.1952	−0.258	15.8	16.1	5.6
75.0	0.0720	−1.62	20.2	49.8	1.5	0.1098	−0.732	17.1	19.8	5.3	0.2260	−0.243	15.0	13.4	4.9
95.8	0.0790	−1.58	20.3	46.5	4.0	0.1217	−0.719	16.9	18.4	5.6	0.2392	−0.237	14.6	12.4	4.9
NaCl, m															
1.020	0.0804	−2.85	60.5	58.1	7.0	0.0569	−1.399	52.7	38.3	23.0	0.0829	−0.505	40.4	38.6	29.6
2.083	0.0357	−2.82	50.2	92.3	3.1	0.0400	−1.325	45.7	44.9	18.1	0.0778	−0.475	35.9	39.4	23.7
4.366	0.0151	−2.90	35.3	133.8	−3.6	0.0250	−1.211	34.9	52.4	11.2	0.0714	−0.428	29.0	39.9	15.7
5.619	0.0118	−2.92	29.3	146.4	−2.4	0.0223	−1.163	30.9	53.5	8.9	0.0717	−0.407	26.3	39.0	12.7

[a] 3.0000 Gc., λ_1 = 13.844 cm., d. = 0.5961 cm.

[b] 9.9987 Gc., λ_1 = 3.989 cm., d. = 0.3244 cm.

[c] 17.0000 Gc., λ_1 = 2.134 cm., d. = 0.1496 cm.

Table II. Dielectric Properties of Phosphoric Acid and Sodium Chloride Solutions

H_3PO_4 Concn., m	ϵ_0	RMS$\Delta\epsilon$	λ_m, Cm.	H_3PO_4 Concn., m	ϵ_0	RSM$\Delta\epsilon$	λ_m, Cm.	NaCl Concn., m	ϵ_0	RMS$\Delta\epsilon$	λ_m, Cm.
0.000	78.3	0.00	1.53	3.000	55.4	0.79	1.80	1.020	62.8	1.15	1.41
0.010	77.8	0.04	1.54	5.000	43.5	1.49	1.76	2.083	52.2	1.38	1.29
0.100	76.3	0.32	1.57	7.500	35.0	1.83	1.69	4.366	37.6	1.43	1.07
0.250	75.1	0.31	1.61	10.000	31.5	1.45	1.63	5.619	32.1	1.88	0.96
0.500	73.5	0.32	1.66	15.000	28.7	1.05	1.52				
0.750	71.8	0.18	1.70	20.000	26.3	1.18	1.43				
1.000	70.2	0.22	1.73	30.000	23.2	1.22	1.29				
1.250	68.2	0.23	1.76	50.000	20.5	1.08	1.14				
1.500	66.3	0.25	1.78	75.000	19.2	1.10	1.14				
2.000	62.4	0.53	1.80	95.800	19.6	1.50	1.21				

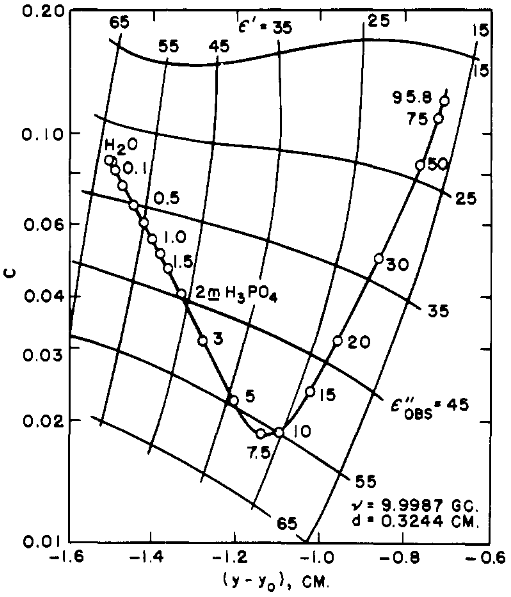


Figure 4. Survey chart for 10-Gc. data

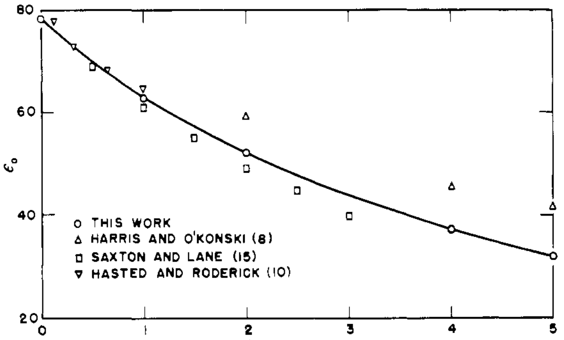


Figure 5. Static dielectric constants of sodium chloride solutions

Davidson-Cole arc function (*6*) gave unrealistic values for the static constants, but those by the Cole-Cole arc function (*3*) or the simpler Debye circle function (*3*) gave reasonable values that agreed within the limits of error of the measurements. The Debye circle function was selected for its simplicity; it is the equation of a circle that has its center on the ϵ' axis and passes through the observed points to intersect the ϵ' axis at ϵ_∞ (the optical constant) and ϵ_0 (the static constant).

On separation of the complex constant ϵ^* of the Debye equation

$$\epsilon^* = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)/(1 + j\omega\tau_m)$$

into its real and imaginary parts it becomes

$$\epsilon' = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)[1 + (\lambda_m/\lambda)]}{1 + (\lambda_m/\lambda)^2}$$

$$\epsilon''_{ac} = \frac{(\epsilon_0 - \epsilon_\infty)(\lambda_m/\lambda)}{1 + (\lambda_m/\lambda)^2}$$

where

τ_m is the relaxation time when the absorption is maximum
λ_m is the wavelength of maximum absorption
λ is the wavelength of the frequency at which measurements were made
$\lambda_m/\lambda = \omega\tau_m$
$\omega = 2\pi\nu$

Each interferometer was standardized with conductance water on the basis of the static dielectric constant, 78.303, of Malmberg and Maryott (*12*) and the absorption-dispersion described by Grant, Buchanan, and Cook (*7*) in terms of the Cole-Cole arc function (*3*) in which the distribution parameter, α, was 0.02 radian. When it was found that the simpler Debye function (*3*), in which $\alpha = 0$, expressed the data adequately, the standardization was recalculated. With each of these functions, ϵ_∞ was 4.5, ϵ_0 was 78.3, and λ_m was 1.53 cm.

It was assumed that the optical constant of all the solutions was the same as that of water, 4.5. Calculations showed that change in the optical constant from 4.5 to 8.5 changed the value of the extrapolated static constant by only about 1 unit.

For each acid solution the Debye circular arc was calculated that passed through the fixed optical constant and had the best least-squares fit to the experimental points. The resulting values of ϵ_0 are shown in Table II; median values of the wavelengths of maximum absorption (calculated from the observations at the two higher frequencies) and values of RMS $\Delta\epsilon$, the square roots of the averages of the squares of the radial distances of the experimental points from the extrapolation circle for each solution, are listed also.

Measurements of the dielectric properties of sodium chloride solutions were made as a check on the reliability of the method. The results are included in Tables I and II and compared in Figure 5 with published data.

In the measurements on the phosphoric acid solutions at 3 Gc., the values of ϵ''_{obs} for the 15 and 20 *m* solutions were smaller than the corresponding values of ϵ''_{dc}, an anomaly that resulted from the poor resolution of the measurements at low frequency on high-loss solutions.

In the measurements on phosphoric acid solutions, the values of ϵ_0 for solutions 0.01 to 3*m* probably are in error by no more than 3 units, and for solutions as concentrated as 75*m*, by no more than 5 units. For the sodium chloride solutions, the values of ϵ_0 for the 1 and 2*m* solutions probably are in error by no more than 1 unit, and for the two more concentrated solutions, by no more than 3 units.

When the 3-Gc. experimental points alone were extrapolated to zero frequency by the Debye function, the resulting static dielectric constants agreed within the limit of experimental error with those obtained by extrapolation from three frequencies.

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